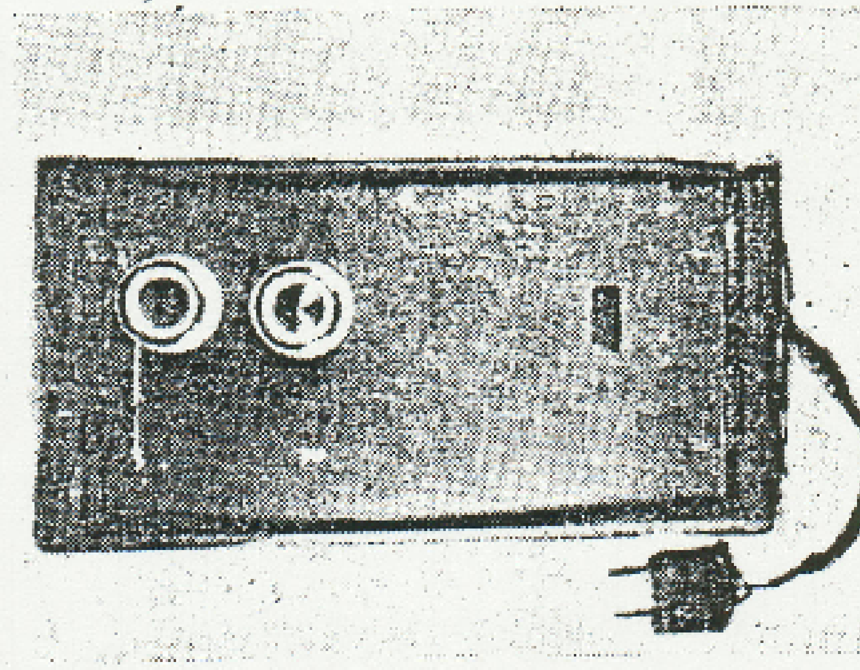
INVENTION INTELLIGENCE (INDIA)



A MYSTERIOUS ORE

By

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The author came to know of the existence of an electric stone" in the hills round about Bhilwara in Rajasthan. The author was told that this stone has the extraordinary property of conducting electricity and due to the presence of this stone in the Bhilwara area it was claimed that neither Bhilwara nor the neighouring villages have ever been struck by lightening (thunder) even in the midst of rainy season. The author, as a chemist, knew that most of the naturally occurring stones are perfect insulators, for example marble, alabestor, slate, granite, silimanite etc. To taste the extraordinary property of this natural occurring stone the author procured about 25 kilograms of stone from the Bhilwara area and he examined the physical, chemical and electrical properties of the stone.

Physical and Chemical Nature of the Stone.

The stone is a grey-coloured crystalline substance with a steel grey metallic lustre found in the ignious rocks (buff coloured granite) of the Aravalli range of mountains. Its specific gravity is quite high and varies between 6.8 and 7.2. Its melting point is about 11000° C, and the molten substance on cooling solidifies to the original crystalline material, the size of its crystals depending on the rate of cooling. The crystals belong to the cubical system the rock is polycrystalline, and the dimensions of the crystals of the original rock vary between 0.12 to 0.24 mm. on sides. The bed-rock of the stone is a buff-coloured granite, which is usually the principle rock of the Aravalli range of mountains. Normally the colour of the stone is steel-grey, but in some specimens, particularly those containing larger crystals, the colour is smokey-grey, slate-grey or almost black. The hardness of the stone is about 4.5 on Mohr's scale, making it almost at par with such hard substances as quartz, garnet, agate, chalcedony and topaz. Photographic reproductions of the stone are shown in Plates I, II. In Plate III, the stone is shown with portions of the bed-rock (buffcoloured granite), attached. Such ingress of granite matrix within the crystalline stone is a fairly common phenomenon, and is what can be expected in view of the crystalline stone having grown out of a molten ignious rock like granite by the normal process of crystallisation. In an uncut and unpolished stone however, these two different materials are difficult to distinguish, as they have practically the same colour in the freshly fractured surface.

Chemically, the stone is an argenti-zinciferrous-galena, containing lead sulphide as the principle ingredient. It is very resistant to chemical reagents, but can be dissolved in fuming nitric acid (sp. gr. 1.51), leaving behind a small insoluble residue. In molten potassium hydroxide, however, it dissolves completely without leaving any residue. Cold concentrated nitric acid (sp. gr. 1.42, at 10° C) dissolves the substance only partially without affecting the lead sulphide, but removing atleast the zinc and the silver completely. The

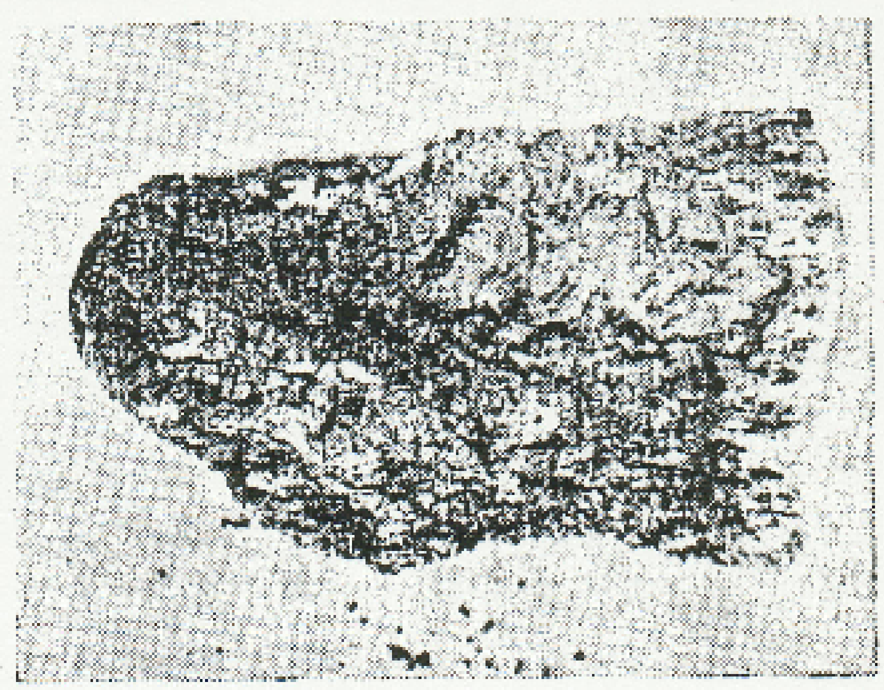

Plate I

following table gives the complete analysis of three representative samples of the stone :—

Table I

Chemical Aanalysis of the Stone.

Constituents	Sample I (%)	Sample II (%)	Sample I I (%)
Lead	79.1	79.3	79.2
Sulphur	14.3	14.6	14.5
Zinc	2.3	2.3	2.7
Silver	1.8	1.6	1.6
Copper	0.16	0.18	0.16
Iron	0.23	0.25	0.25
Aluminium	0.12	0.26	0.31
Antimony	0.25	0.37	0.26
Calcium	nil	nil	nil
Magnesium	nil	nil	nil
Acid insoluble	1.8	1.8	1.8

The stone on treatment with hot fuming nitric acid (sp. gr. 1.51) is almost completely dissolved, leaving a small quantity of a crystalline residue (1.8%). In the oxy-acetylene flame the residue could be melted to a white-hot globule in a small graphite crucible, and it congealed on cooling to a small hard ball with a steel-grey colour and a bright metallic lustre. Sufficient quantity of this insoluble substance was obtained for analysis which is given below :—

Table II.

Analysis of the Acid-insoluble Residue.

Iron	23.49%
Aluminium	0..0%
Manganese	0.14%
Calcium	0 27%
Magnesium	0.13%
Titanium	0.08%
Carbon	0.45%
Phosphorus	0.02%
Silicon	75.01%
Sulphur	0.01%

This acid-insoluble substance which appears to be chemically inert to most reage.its, however, reacts quickly with concentrated caustic soda and potash, and in the molten alkalies dissolves completely without leaving any residue. After melting and congealing, the residue had the same crystalline structure as the original stone, but its semi-conducting electrical properties appeared to be somewhat less than those of the original stone. Further examination of this material is in progress.

The powdered stone on treatment with cold concentrated nitric acid (Sp. gr. 1.42, at 10°C) gets partially dissolved, and after filtration and thorough washing with

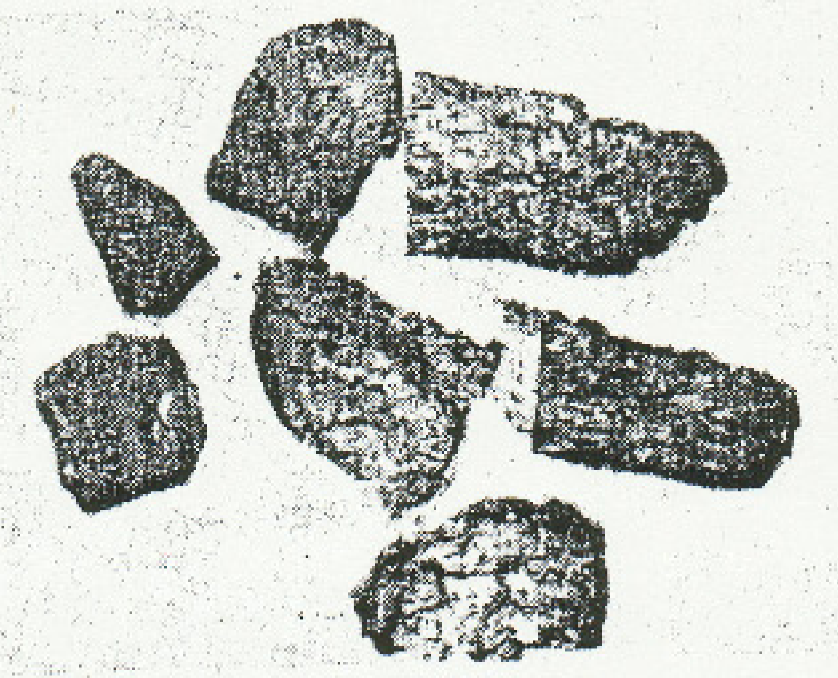

Plate II

ice-cold distilled water and drying at 110°C, the residue had the following composition :—

Table III

Composition of Cold Nitric acid-insoluble Residue.

Lead	83.27%
Sulphur	13.32%
Copper	0·12%
Antimony	0.24%
Iron	0.28%
Aluminium	0.64%
Zinc	nil
Silver	nil
Calcium	nil
Magnesium	nil
Acid insoluble	2.20%

This substance was melted in the oxy-acetylene flame in a graphite crucible and the white-hot molten mass on cooling, congealed to a grey-coloured crystalline mass with metallic lustre, exactly similar to the original stone in appearance and general chemical and physical properties. Its electrical properties were found to be practically identical with those of the original stone. Thus silver and zinc having been eliminated as possible causative factors for the semi-conductive properties of the stone, the only other major impurity that remains to be considered in this connection is the insoluble matter that remains behind after the stone is dissolved in hot fuming nitric acid. This insoluble matter has already been mentioned before and its analysis given. It appears to have very interesting semi-conducting properties which are practically the same or only slightly less than those of the original stone. Further investigation of this material is in progress.

Electrical Properties of the Stone

The most remarkable property of the stone is its electrical conductivity, which appears to be similar to that of metallic lead. When tested with an ohmmeter and a 1.5 volt dry battery, the conductivity appears to be of the order : r = 25–45 ohms/cm. for large lumps, at the ordinary temperature (22°C). Another peculiarity is that the conductivity increases with the rise of temperature, and at 100°C, the value becomes: r = 10·7–17 ohms/cm. This is just the reverse of the normal conductivity of metals, which falls off in value with the progressive rise in temperature. This indicates the semi-conducting nature of the stone, which is confirmed by the following experiments : A thin slice of the stone was prepared (thickness 2 mm.) by first rough grinding a small block of the stone on an electrically driven carborundum disc grinder, then on a flat carborundum slab by hand and finally on a jewellers lapping machine. With a forward bias at 6 volts between two sharp pointed silver electrodes placed at a distance of 1 cm. from each other, the resistance was 340–500 ohms. With a reverse bias at the same voltage, the resistance was 15–65 kilo ohms. With the points placed at a distance of 2mm. from each other, the forward resistance was 85–160 ohms, and the reverse resistance 85–350 kilo ohms. When reduced to a thickness of 0.18 mm. (thickness of an average crystal of the stone) by a special process the values became : forward resistance : 50–120 ohms/mm., reverse resistance :-105–500 kilo ohms/mm. Thus the semi-conducting nature of the stone was established, and the quality of semi-conduction was such as could possibly lead to the preparation of diodes and transistors. That the stone is a good rectifier for the detection of broadcast radio waves has already been mentioned. But how far this rectifying (demodulating) property reached amongst the various frequency bands of modern radio transmissions, and so many other electronic properties of the stone, could only be tested by the preparation of diodes and transistors from the stone, and carefully testing such devices on well-designed receiver circuits. The present author, therefore, turned his attention to the prepration of such devices.

From the mathematical point of view, the forward conductivity provided by conduction electrons will be determined by the number of electron and the ease of their movement in an applied electric field. The latter is described by their 'mobility', which is the drift velocity of the carriers in cm./sec. in a field of 1 volt/cm. Thus the equation becomes : $\delta n = \mu n\, qn$
where δn is the conductivity due to the electrons in (ohms. cm.)$^{-1}$ μn is cm^2/volt. sec., and q is 1.60×10^{-19} coulombs.

The reverse conductivity, that is conductivity due to 'holes'[1] is given by the equation : $\delta p = \mu p\, qp$ and the total conductivity by : $\delta = 1/\rho = q(\mu_n n + \mu_p p)$ where μ is the resistivity. Often either n or p predominates, and one of the terms on the right hand side of the equation may be neglected. In some materials a large difference between μn and μp produces this result also.

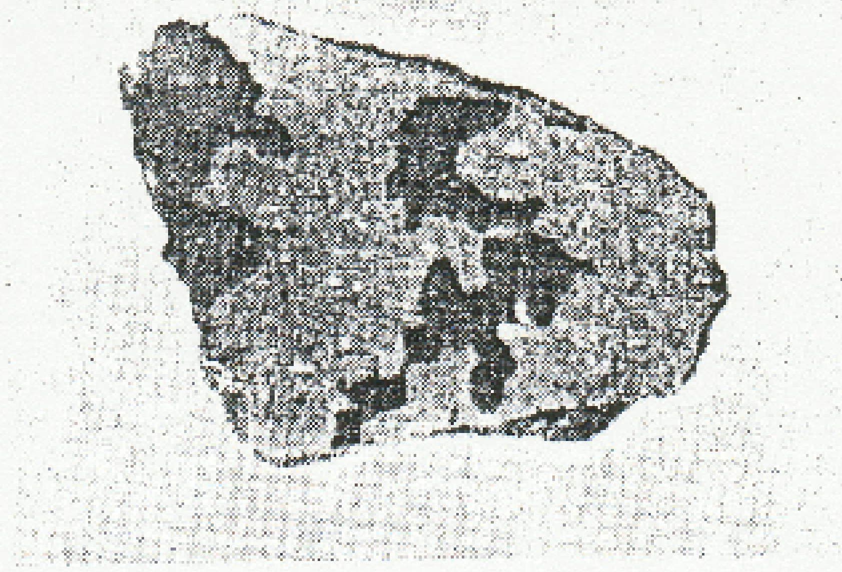

Plate III

The temperature dependence of the conductivity of semiconductors is one of the most striking and characteristic of their properties. The principle changes in the conductivity of a given sample, with temperature, result from changes in the carrier concentration, although the mobility also varies with the temperature. At low temperature the conductivity is low, because most of the carriers are frozen out on the donor centres. As the temperature rises, the degree of ionisation of the donors increases, and the rising carrier concentration results in a rapidly increasing conductivity. The increasing thermal agitation of the crystal lattice leads to a shorter distance for the carriers to travel between collisions within the lattice, and the carriers travel faster at higher temperatures, thus shortening the time between collisions.

Another important electrical phenomenon to which the stone from Rajasthan readily responds, is the Hall's Effect[3], which is carried out as follows : an electric current is passed through the material and a magnetic field is applied at right angles to the direction of the current flow. A transverse voltage develops, the sign of which depend upon the material being tested. The voltage is directly proportional to the thickness of the material in the direction of the magnetic field. The proportionality constant is called the Hall's Coefficient R, and this is determined by the equation :

$$V = \frac{10^{-8}\, RIH}{t}$$

where I is in amperes, H in gauss, t in cm., V in volts and R in cm³/coloumbs. Hall's coefficient for the stone has been found to vary between the values of 0.039 ev. to 0.053 ev. The value for well known semi-conductors like germanium-indium = 0.058 ev., and of silicon-arsenic = 0.049 ev.

The stone being essentially sulphide of lead in a crystalline form, it was reasonable to assume that it would mainly correspond to pure lead sulphide so far as its semi-conducting properties are concerned. But the semi-conducting properties of the stone were found to be over a million times greater than those of pure lead sulphide. Hence it was not the lead sulphide (main constituent) that really mattered in the semi-conduction. The impurities present in the stone must be the deciding factor in this connection. Amongst the impurities, two are present in comparatively large proportions, namely zinc and silver. Both of them, however, can be practically completely removed from the powdered stone by treatment with cold (10°C) concentrated nitric acid. The residue left after this treatment contains the entire amount of the lead sulphide originally present in the stone. This can be melted in an oxyacetylene flame and the molten material allowed to crystallise by slow cooling. The crystalline stuff thus obtained was found to have the same semi-conducting properties as the original stone. Thus the impurities like zinc and silver are not responsible for producing the the extraordinary semi-conducting properties of the lead sulphide in the stone. What could be the cause then?

The only other major impurity present in the stone is the nitric acid-insoluble matter (1.8%) about which mention has already been made before. That it has practically the same semi-conducting property as the original stone has is really very remarkable. It is being further investigated.

Amongst other impurities present in the stone in minute quantities are: copper, aluminium, iron, and antimony. The first three are already known to have no influence on the semi-conductance of such well-known materials as germanium and silicon. But the case of antimony is different. The trivalent metals like arsenic and antimony, and to a smaller extent, bismuth, have profound influence on the semi-conduction of both germanium and silicon, when added in minute proportions. Could it be antimony then which is largely influencing the semi-conducting properties of the stone? Unfortunately, this question can not be answered at the present stage of progress of this investigation.

The semi-conducting properties of the stone in large lumps are of the order: forward resistivity = 25-45 ohms/cm. reverse resistivity = 5-75 kiloohms/cm. When reduced to thickness of 2 mm. by fine and careful grinding, the values are: f.r.-340-500 ohms/cm. rr. 15-65 kiloohms/cm. When reduced to the thickness of an average crystal (0.18 mm.) by a special process, the values become; f.r. = 50-120 ohms/mm., rr.-105-500 kiloohms/mm. The conductance of the stone increases with rise of temperature and it also responds to Hall's Effect. From all these it was concluded that the stone is an extraordinary semi-conducting material and should be an excellent substance for the preparation of good quality transistors and efficient radio receivers.

The stone not being a metal like germanium from which most of the modern junction transistors are made, it became obvious from theoretical considerations that only 'point-contact' transistors could be made from it. Besides, the stone being polycrystalline, it was natural to expect the formation of both P-N-P and N-P-N transistors from it because the junctions between adjacent crystals would be oppositely charged and the tri-contact-points of the transistor would come in contact with the different junctions in all possible permutations and combinations. In actual practice both these expections have been realised and all the possible varieties of transistors obtained.

These RS transistors prepared by the present author have been made into radio receivers to receive broadcasts in the medium, and short wave bands (wavelengths 200-500 m, 50-180 m and 13—50m, respectively). The best results have been found to be obtained when the receivers are constructed on the Regenerative and Super-Regenerative principles. Receivers constructed on the Super-Heterodyne principle, although working fairly satisfactorily, give a certain amount of background noise (hum) due to non-matching of the intermediate frequency transformers, which unfortunately are not commercially available for this entirely new type of RS transistors. *(To be Contd.)*